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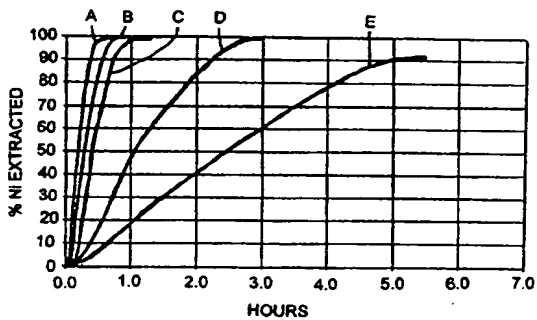
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(54) PRODUCTION DE POUDRE DE NICKEL ACTIVE ET TRANSFORMATION DE CELLE-CI EN NICKEL-CARBONYLE

(54) PRODUCTION OF ACTIVE NICKEL POWDER AND TRANSFORMATION THEREOF INTO NICKEL CARBONYL

(57)

Active nickel powder is produced by reducing a nickel chloride containing salt having a high surface area with hydrogen gas at a temperature above 300.degree.C. The obtained active nickel powder can be rapidly converted into nickel carbonyl by reaction with carbon monoxide gas at atmospheric or superatmospheric pressure and in the absence of conventional carbonylation catalysts.





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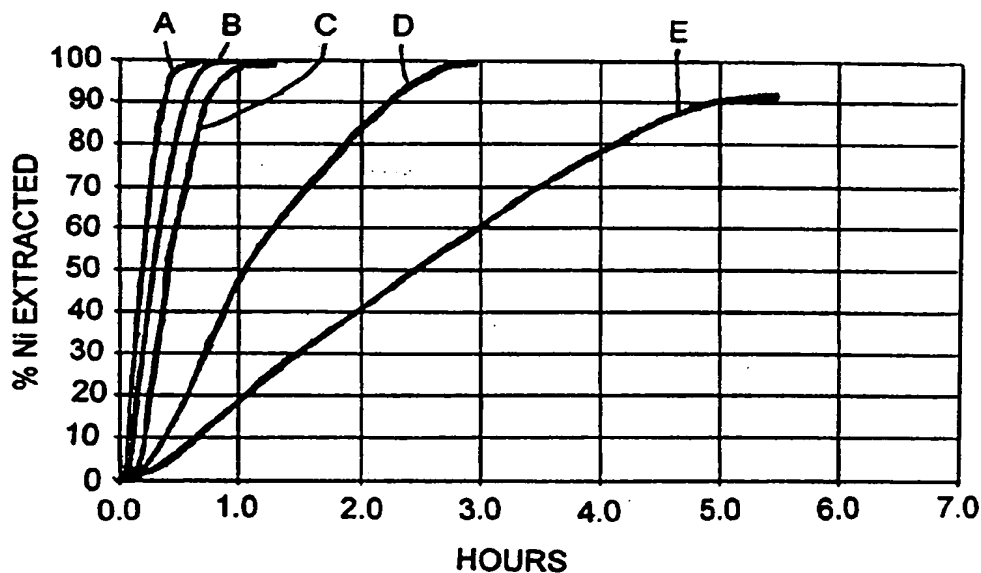
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(54) Titre : PRODUCTION DE POUDRE DE NICKEL ACTIVE ET TRANSFORMATION DE CELLE-CI EN NICKEL-CARBONYLE

(54) Title: PRODUCTION OF ACTIVE NICKEL POWDER AND TRANSFORMATION THEREOF INTO NICKEL CARBONYL



(57) Abrégé/Abstract:

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### ABSTRACT OF THE DISCLOSURE

Active nickel powder is produced by reducing a nickel chloride containing salt having a high surface area with hydrogen gas at a temperature above 300°C. The obtained active nickel powder can be rapidly converted into nickel carbonyl by  
5 reaction with carbon monoxide gas at atmospheric or superatmospheric pressure and in the absence of conventional carbonylation catalysts.

## **PRODUCTION OF ACTIVE NICKEL POWDER AND TRANSFORMATION THEREOF INTO NICKEL CARBONYL**

### **FIELD OF THE INVENTION**

This invention relates to the production of an active nickel metal powder  
5 suitable for transformation into nickel carbonyl. Moreover, it relates to the  
transformation of the active powder into nickel carbonyl by reaction with carbon  
monoxide at atmospheric or superatmospheric pressure and in the absence of  
conventional carbonylation catalysts.

### **BACKGROUND OF THE INVENTION**

10 It is well known to use the Mond process for the extraction of nickel from  
ores, mattes, residues, or similar compounds containing nickel, in which such  
compounds are reduced to yield finally divided metallic nickel which is then treated  
with carbon monoxide to produce nickel carbonyl that can then be decomposed to  
yield nickel. Various improvements to this process have been suggested to increase  
15 the rate of nickel carbonyl production and thus render the overall process more  
economical.

For example, in Canadian Patent No. 322,887 it is suggested to add to the  
reaction chamber producing nickel carbonyl, a compound containing sulphur,  
selenium or tellurium in "active form", such as nickel sulphide, nickel selenide or  
20 nickel telluride and carrying out the carbonylation reaction in the absence of oxygen.  
The preferred additive is nickel sulphide and it is added so that the amount of active  
sulphur in the reaction chamber lies between 0.2% and 5% by weight. It, therefore,  
acts as a catalyst to promote the carbonylation reaction.

In U.S. Patent No. 4,045,541 another improvement is disclosed according to which a metal, such as iron, copper or cobalt, which forms sulphides more easily than nickel at 200°C, is admixed with the material comprising elemental nickel, such as nickel oxide, which is then subjected to carbonylation and sulfidation.

5           British Patent No. 649,988 discloses a process for the manufacture of nickel carbonyl by reacting an aqueous solution of a nickel salt, such as nickel chloride or nickel sulphate, with an alkaline reacting substance, producing a nickel compound which is treated in aqueous solution or suspension with carbon monoxide under superatmospheric pressure of at least 50 atmospheres and at elevated temperatures of  
10           at least 70° C, and in the presence of a minor amount of nickel sulphide or cyanide as a catalyst.

All the above prior art processes require the presence of various additives or carbonylation catalysts and/or the use of superatmospheric pressure and elevated temperature to achieve satisfactory rates of nickel carbonyl production.

15           There is thus a need for a simplified production of nickel carbonyl from nickel salts.

#### OBJECTS AND SUMMARY OF THE INVENTION

It is an object of the present invention to produce active nickel powder from nickel chloride or nickel salt mixtures containing nickel chloride, which active  
20           powder is capable to react with carbon monoxide gas at atmospheric or superatmospheric pressure to yield nickel carbonyl.

It is a further object of the present invention to transform the active nickel powder produced from nickel chloride or nickel salt mixtures containing nickel chloride into nickel carbonyl at rapid and commercial rates without addition of

carbonylation catalysts or promoters, such as used in the prior art.

Other objects and advantages of the present invention will become apparent from the following description thereof.

In essence, it has been found that nickel salts containing 5% to 100% of nickel chloride and having a high surface area can be rapidly reduced to active nickel powder by reaction with a reducing hydrogen gas at a temperature above 300°C, and preferably between 300°C and 600°C. The reducing hydrogen gas should normally contain at least 20% by volume of H<sub>2</sub>, but is preferably pure hydrogen. The resulting activated nickel powder can then be reacted with CO gas at atmospheric pressure and temperatures of 20°C to 60°C, preferably about 50°C, to produce nickel carbonyl - Ni(CO)<sub>4</sub>, with a yield close to 100%. The activated nickel powder can also be reacted with CO at superatmospheric pressure and elevated temperature, if desired. The carbonylation reaction with CO gas is simple and effective, requiring no catalysts or other promoters.

When other nickel salts, such as nickel carbonate or nickel sulfate are treated in the same manner, namely by reaction with H<sub>2</sub> gas at 300°C - 600°C, essentially no active nickel powder is produced. However, surprisingly, when such salts are admixed with at least 5% by weight of NiCl<sub>2</sub>, the entire admixture produces active nickel powder. The Ni recoveries obtained with the admixture of NiCO<sub>3</sub> and NiCl<sub>2</sub> are in the range of 95-100% and the recoveries obtained with the admixture of NiSO<sub>4</sub> and NiCl<sub>2</sub> are usually slightly lower, but still in a very appreciable range of 85-90%, probably due to the formation of some nickel sulphide which does not carbonylate.

When reference is made to nickel chloride, it can be either dehydrated or in the form of hydrates, such as NiCl<sub>2</sub>·6H<sub>2</sub>O. Moreover, when reference is made to

nickel salts, they can also be in hydrated form and/or combined with other nickel compounds, such as nickel hydroxide or the compound called zaraitite -  $2\text{Ni}(\text{OH})_2 \cdot \text{NiCO}_3 \cdot 4\text{H}_2\text{O}$ .

5 The starting material should have a high surface area in excess of  $10\text{m}^2/\text{g}$ , and preferably between 35 and  $100\text{m}^2/\text{g}$ .

The active nickel powder produced in accordance with the present invention can be exposed to air for a short period of time and still remain active. It can also be maintained under inert gas, such as argon, for several days without losing its activity. Another useful feature of this powder is that once the active nickel powder loses its  
10 activity due to storage, in the absence of oxygen, it can be re-activated by exposing it to  $\text{H}_2$  gas at about  $150^\circ\text{C}$  or higher temperatures. If the active nickel powder loses its activity due to storage in the presence of oxygen, it can be re-activated by exposing it to  $\text{H}_2$  gas at a temperature of  $300^\circ\text{C}$  to  $600^\circ\text{C}$ . This is an important advantage of the present invention because it enables to perform the carbonylation reaction completely  
15 separately and at a different location from the reduction reaction that produces the active nickel powder.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a graph showing nickel extraction from active nickel powder produced by reduction of nickel chloride;

20 Fig. 2 is a graph showing nickel extraction from active nickel powder where treatments were made on various  $\text{NiCl}_2$  materials at different temperatures.

Fig. 3 is a graph showing nickel extraction from nickel powder produced by reduction of nickel carbonate; and

Fig. 4 is a graph showing nickel extraction from active nickel powder

produced by reduction of an admixture of nickel carbonate and nickel chloride.

Fig. 5 is a graph showing nickel extraction at superatmospheric pressure and elevated temperature from active nickel powder of the present invention as compared to regular nickel powder of the prior art.

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#### DETAILED DESCRIPTION OF THE INVENTION

Examples of preferred but non-limitative embodiments will now be described with reference to the appended drawings. In these examples, tests were carried out by first reducing a pre-dried small sample (25mg) of finely divided nickel chloride and of nickel carbonate alone and in admixture with nickel chloride respectively. The reduction was carried out in hydrogen at 500°C. The obtained nickel powder was then cooled to 200°C and the reactive gas switched from hydrogen to carbon monoxide at a flow rate of 10ml/min. The sample was then further cooled to 50°C. Weight loss was monitored over time using computer software. The weight loss was confirmed with TGA (thermogravimetric analysis) measurements, and the residue was dissolved in acid and analyzed for nickel to give a complete mass balance. The obtained nickel metal powder reacted with CO to form volatile nickel carbonyl gas which was removed and decomposed at high temperature into a pure nickel product as in known in the art.

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#### EXAMPLE 1

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In this example,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  was pre-dried at 170°C in air and treated as described above. Nickel extraction of 99.6% was obtained in 45 minutes as illustrated by the curve in the graph of Fig. 1 and by curve B in the graph of Fig. 2.

The same procedure as above was repeated with a sample of  $\text{NiCl}_2$  pre-dried at 300°C in  $\text{N}_2$ . Ni extraction of essentially 100% was obtained in about 30 minutes as



illustrated by curve A in the graph of Fig. 2.

The same procedure was repeated with another sample of  $\text{NiCl}_2$  pre-dried at  $170^\circ\text{C}$  in air. Ni extraction of essentially 100% was obtained in about 1 hr. as illustrated by curve C in the graph of Fig. 3.

5        The same procedure was repeated but using a temperature of  $600^\circ\text{C}$  -  $800^\circ\text{C}$  for reduction in hydrogen. In this case, essentially full extraction was reached after about 2.5 hours, as illustrated by curve D in the graph of Fig. 2. This shows that temperatures higher than  $600^\circ\text{C}$  actually slow down the extraction and there is no practical reason to use them. The present invention is, however, not limited to  
10        temperatures below  $600^\circ\text{C}$ .

The same procedure was repeated using anhydrous  $\text{NiCl}_2$  without pre-drying. In this case, only about 90% of extraction was achieved after about 5 hrs, as illustrated by curve E in the graph of Fig. 2.

The above experiments indicate that changes in drying temperatures and  
15        hydrogen reduction temperatures and in the composition of the nickel chloride may lead to variations in extraction rates and the speed of achieving the extractions.

#### EXAMPLE 2

In this example, the procedure described above was repeated but using  $\text{NiCO}_3$  as the starting material. As shown by the curve in the graph of Fig. 3, a very poor  
20        extraction rate of less than 20% was achieved after about 6 hours. It is obvious, therefore, that  $\text{NiCO}_3$  alone did not produce an active nickel powder.

#### EXAMPLE 3

The procedure of Example 2 was repeated but with replacement of the starting material with a mixture of  $\text{NiCO}_3$  and  $\text{NiCl}_2$  in a proportion of 3:1. This gave an

essentially 100% recovery of Ni in less than 1 hour as shown by the curve in the graph of Fig. 4.

Other amounts of mixture blends of nickel carbonate and nickel chloride were tested and good results were obtained starting with about 5% by weight of  $\text{NiCl}_2$  in the mixture. It was found, however, that the most beneficial results are obtained when the amount of chloride in the mixture is between 20 and 25% by weight based on nickel. Moreover, it was found that the higher the surface area of the mixed solids, the faster the extraction of nickel by carbonylation, with optimum results being obtained when the surface area is 80-100  $\text{m}^2/\text{g}$  and the amount of  $\text{NiCl}_2$  is such as to give 20-25 wt%  $\text{Cl}/\text{Ni}$ . Thus, the presence of  $\text{NiCl}_2$  in admixture with other nickel salts, including possible other compounds that may be present with such salts, produces a satisfactory and rapid conversion of the total nickel present in such mixtures into active nickel.

Larger scale tests, using samples of up to 300g, have also been carried out and gave similar results as those described in the above examples, although with conversion times of 3 to 6 hours.

#### EXAMPLE 4

A 10g sample of active nickel powder produced in accordance with the present invention was subjected to carbonylation with CO gas in a small vertical reactor at 300 psi (20 atm) and 85°C and resulted in essentially 100% of Ni extraction in less than 10 hours, as shown by curve F in Fig. 5.

Another 10g sample of non-activated nickel powder was treated in the same manner with CO gas at 300 psi and 85°C, and resulted in a conversion to Ni in over 20 hours as shown by curve G in the Fig. 5.

As previously mentioned, it is already known in the art to carbonylate Ni powder with CO gas at superatmospheric pressures and at elevated temperatures above 70°C. The present example shows that when such known carbonylation is carried out using the active nickel powder of the present invention, a considerable  
5 reduction in the time of Ni extraction is achieved.

It should be noted that the invention is not limited to the specific embodiments and examples described above, but that various modifications obvious to those skilled in the art can be made without departing from the invention and the following claims.

**CLAIMS**

1. Method of producing an active nickel powder which comprises reducing a nickel salt containing 5% to 100% by weight of nickel chloride and having a surface area in excess of  $10\text{m}^2/\text{g}$ , with a reducing hydrogen gas, at a temperature above  
5 300°C.
2. Method according to claim 1, in which the said nickel salt is nickel chloride.
3. Method according to claim 2, in which nickel chloride is in the form of its hydrates.
4. Method according to claim 1, in which the nickel salt is a mixture of nickel  
10 carbonate and nickel chloride.
5. Method according to claim 4, in which nickel carbonate is in the form of zaraitite -  $2\text{Ni}(\text{OH})_2 \cdot \text{NiCO}_3 \cdot 4\text{H}_2\text{O}$ .
6. Method according to claims 4 or 5, in which the amount of nickel chloride is such as to produce 20-25% by weight of chloride based on nickel in the mixture.
- 15 7. Method according to any one of claims 1 to 6, in which the surface area of the nickel salt is between 35 and  $100\text{m}^2/\text{g}$ .
8. Method according to any one of claims 1 to 7, in which the hydrogen containing gas is pure hydrogen gas.
9. Method according to any one of claims 1 to 8, in which the reducing reaction  
20 is carried out at a temperature of 500°C.
10. Method according to any one of claims 1 to 9, wherein if the active nickel powder becomes de-activated due to storage in the absence of oxygen, it is re-activated by exposing it to  $\text{H}_2$  gas at a temperature of at least about 150°C.

11. Method according to any one of claims 1 to 9, wherein if the active nickel powder becomes de-activated due to storage in the presence of oxygen, it is re-activated by exposing it to  $H_2$  gas at a temperature between  $300^{\circ}C$  and  $600^{\circ}C$ .
12. Method according to any one of claims 1 to 9, further comprising reacting the  
5 active nickel powder with CO gas at atmospheric pressure and at a temperature of  $40^{\circ}C$  -  $60^{\circ}C$  to produce nickel carbonyl.
13. Method according to any one of claims 1 to 9, further comprising reacting active nickel powder with CO gas at a superatmospheric pressure and an elevated temperature to produce nickel carbonyl.
- 10 14. Active nickel powder capable of being rapidly converted into nickel carbonyl by reaction with carbon monoxide gas at atmospheric or superatmospheric pressure, said powder being the result of reduction of a nickel chloride containing salt with a high surface area in excess of  $10m^2/g$  by hydrogen at a temperature above  $300^{\circ}C$ .
- 15 15. Active nickel powder according to claim 14, in which the nickel chloride containing salt is nickel chloride.
16. Active nickel powder according to claim 14, in which the nickel chloride containing salt is a mixture with a quantity of nickel chloride in the mixture being such as to produce 20-25% by weight of chloride based on nickel.

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$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$

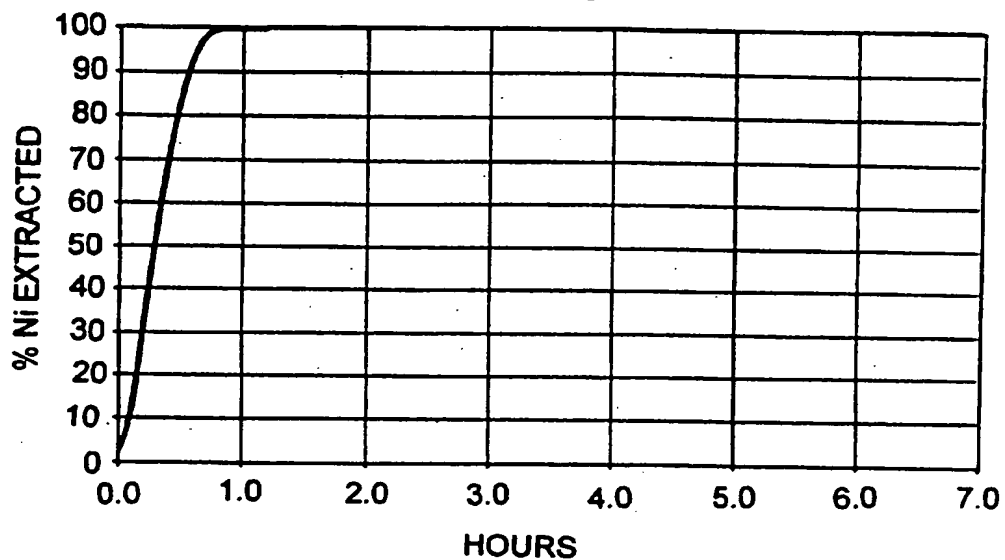


Fig. 1

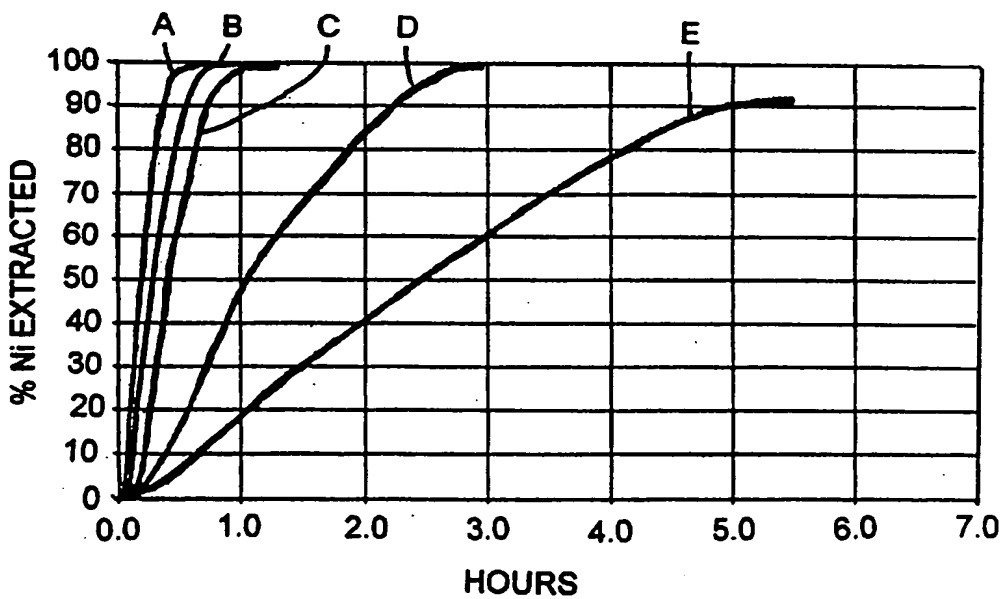


Fig. 2

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$\text{NiCO}_3$  - no addition of  $\text{NiCl}_2$

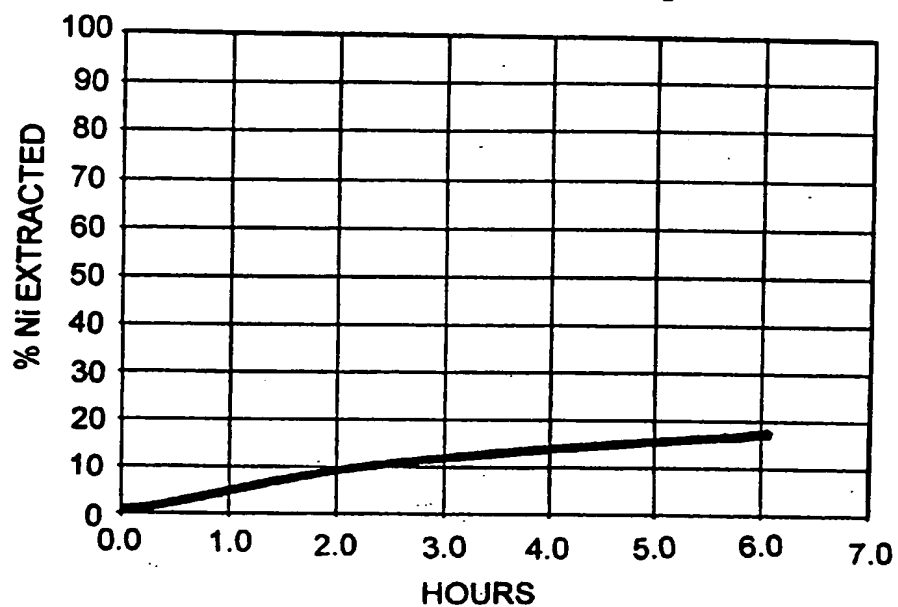


Fig. 3

$\text{NiCO}_3$  -  $\text{NiCl}_2$  (3:1) Mixer Blend

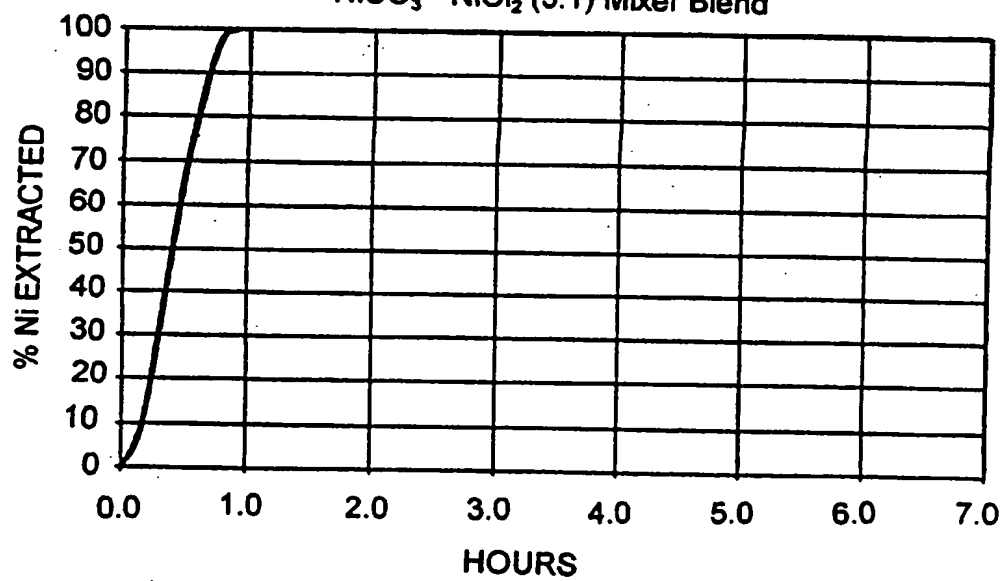


Fig. 4

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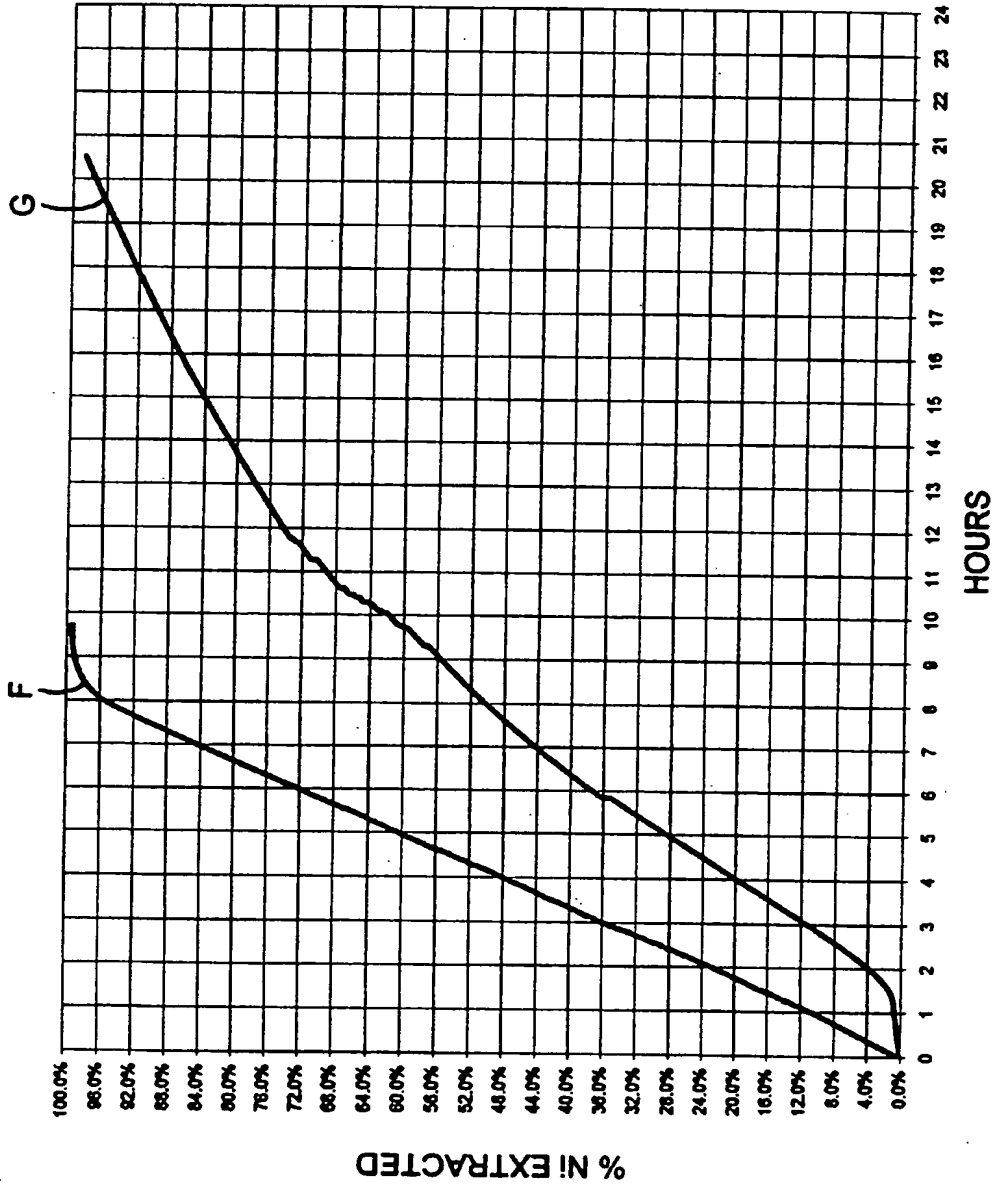


Fig. 5